sistent with the ring size effects and alkyl substituent effects which we discussed. Rerrangement reactions studied in Olah's group showed a strong preference for three- and five-membered ring halonium ion formation.[17] Larsen and Metzner[18] found 8–19 kcal/mol of stabilization in three-membered ring bromonium ions. These authors also found increased sensitivity to methyl stabilization in the three-membered ring, compared to five, indicative of the carbonium ion nature of carbons in the three-membered ring. Our work shows that ^{13}C nmr effects in five-membered rings are well accommodated within a framework which correlates the properties of the halonium ions and other cyclic compounds as a function of structure and ring size.

Experimental Section

Chemicals.—All dihalide precursors to the various ions were either commercially available materials or prepared as described previously.[5] The cyclic sulfides and alkanes whose nmr line positions are listed in Figure 2 also were commercially available.

Preparation of the Ions.—The ions were prepared at 0.6–0.8 *M* concentration levels by procedures mentioned previously.[2,3,5]

Nmr Spectra.—Nmr spectra were obtained on a Varian XL-100-15 spectrometer with accompanying VFT-100-X Fourier transform unit. The line positions for noise-decoupled spectra were read out of the accompanying Varian 620i computer and, after referencing, are accurate to ±0.2 ppm. All halonium ion spectral parameters were measured at −65 to −70° and referenced to carbon disulfide as described in the text. Chemical shifts for the cyclic sulfides and alkanes were measured on 1.0 *M* solutions in carbon tetrachloride at room temperature and were referenced to centered 5-mm tubes of $C_2F_4Br_2$. The $C_2F_4Br_2$ signal was separately shown to be 78.2 ppm upfield from CS_2 in CCl_4 at room temperature. The δ ^{13}C values obtained for the cyclic sulfides and alkanes follow: ethylene sulfide (thiirane), C-2 175.1; trimethylene sulfide (thietane), C-2 166.9, C-3 164.8; tetramethylene sulfide (thiolane), C-2 162.1, C-3 162.9; pentamethylene sulfide (thiane), C-2 163.3, C-3 164.1, C-4 165.7; cyclopropane, 195.4; cyclobutane, 170.0; cyclopentane, 166.9; and cyclohexane, 165.8.[19] Assignments of the various carbon shifts in the sulfur heterocycles was accomplished by heteronuclear hydrogen decoupling while observing the carbon spectrum.

Registry No.—**4**, 22211-89-8; **5**, 22211-90-1; **6**, 22211-91-2; **7**, 33740-96-8; **8**, 33740-97-9; **9**, 33740-98-0; **10**, 33740-99-1; **11**, 22211-92-3; **12**, 23595-67-7; **13**, 22211-93-4.

Acknowledgment.—Support by the National Science Foundation (Grant GP 30683) is gratefully acknowledged.

(17) G. A. Olah, J. M. Bollinger, Y. K. Mo, and J. M. Brinich, *J. Amer. Chem. Soc.*, **94**, 1164 (1972).

(18) J. W. Larsen and A. V. Metzner, *ibid.*, **94**, 1614 (1972).

(19) We are indebted to Dr. P. M. Henrichs for obtaining some of these values.

Uniparticulate Electrophilic Addition to Alkenylidenecyclopropanes[1]

DANIEL J. PASTO,* A. FU-TAI CHEN, GHEORGHE CIURDARU,[2] AND LEO A. PAQUETTE*

Departments of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556, and The Ohio State University, Columbus, Ohio 43210

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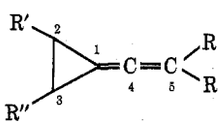
The reaction of a number of substituted isobutenylidenecyclopropanes with chlorosulfonyl isocyanate (CSI) have been investigated for comparison with the reactions of the alkenylidenecyclopropanes with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD). In the previous article the cycloaddition reactions of alkenylidenecyclopropanes with PTAD were described, product formation being proposed to occur *via* a concerted process. A new molecular orbital description of the bonding in the alkenylidenecyclopropanes and the transition states for cycloaddition was advanced to account for the mode of reaction and high reactivity. In contrast to the singular mode of reaction of alkenylidenecyclopropanes with PTAD, the reactions with CSI produce both cyclopropane ring-retained (*N*-chlorosulfonyl-β-lactams formed by electrophilic attack at C_3) and ring-opened (five-membered ring



N-chlorosulfonylimino ethers and *N*-chlorosulfonyl-γ-lactams derived by attack at C_4) products. The ratio of cyclopropane-retained and -opened products is a sensitive function of the number and type of functions attached to the three-membered ring. Product formation is discussed in terms of stabilization of the cationic portion of the dipolar intermediates. It is proposed that the substituent effects on the mode of electrophilic attack arise from stabilization and delocalization of the positive charge developed in the p orbital of C_4 on electrophilic attack at C_5 (which is coplanar with the three-membered ring) with the molecular orbitals of the cyclopropane ring in a manner similar to that described for the ground-state electronic structure of alkenylidenecyclopropanes.

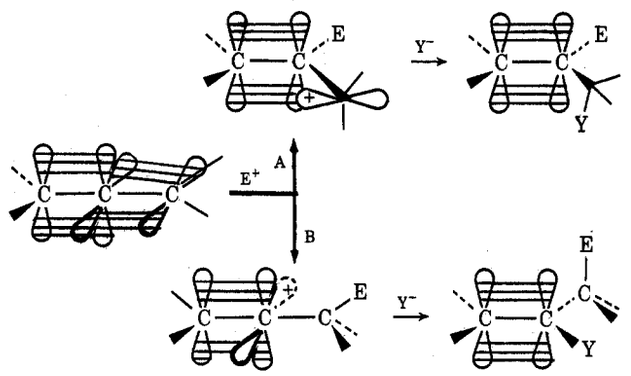
Attack by a nonbridging electrophile on an allene can occur either at the central or the terminal carbon of the cumulene system. Initial bonding at the central carbon produces a nonresonance-stabilized cationic species (path A),[3] the vacant orbital being orthogonal to the proximate π-electron system. Electrophilic attack at a terminal carbon leads to the formation of a vinyl cation (path B).[4] Competition between these two pro-

(1) (a) Cycloaddition Reactions of Cyclopropane-Containing Systems. IV. For the previous paper in this series see D. J. Pasto, A. F.-T. Chen, and G. Binsch, *J. Amer. Chem. Soc.*, **94**, 1553 (1973). Submitted by A. F.-T. C. in partial fulfillment of the requirements for the Ph.D., University of Notre Dame, 1972. (b) Unsaturated Heterocyclic Systems. LXXXVIII. For the previous paper in this series see L. A. Paquette and M. J. Broadhurst, *J. Amer. Chem. Soc.*, **94**, 632 (1972).

(2) Fullbright–Hayes Fellow on leave from the Institute of Chemistry, Cluj, Romania (1971–1972).

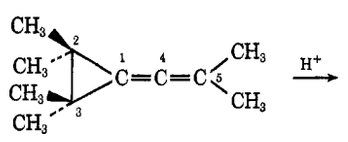
(3) T. L. Jacobs and R. N. Johnson, *J. Amer. Chem. Soc.*, **82**, 6397 (1960); K. Griesbaum, W. Naegele, and G. G. Wanless, *ibid.*, **87**, 3151 (1965); W. L. Waters and E. F. Kiefer, *ibid.*, **89**, 6261 (1967).

(4) For a recent review of this subject see M. Hanack, *Accounts Chem. Res.*, **3**, 209 (1970). See also S. A. Sherrod and R. G. Bergman, *J. Amer. Chem. Soc.*, **93**, 1925 (1971); D. R. Kelsey and R. G. Bergman, *ibid.*, **93**, 1941 (1971).



cesses is sensitive to the degree of substitution on the allene chromophore. For example, allene enters into reaction by preferential bonding at a terminal carbon,[5] while tetramethylallene exhibits reactivity predominantly at the central carbon.[6]

In this context it is interesting to note that electrophilic attack on alkenylidenecyclopropane **1** occurs preferentially at C_5.[7,8] Crandall[7] has attributed the



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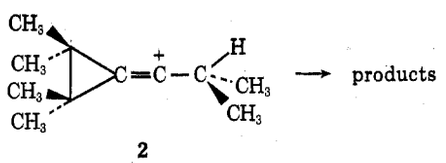


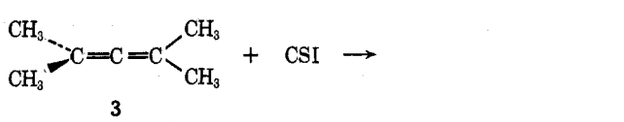
2

apparently enhanced stabilization of the cationic species **2** to its particularly unique geometry in which the σ bonds of the cyclopropane ring are perfectly bisected by the residual π orbitals, a particularly favorable orientation.[9] Production of cation **2** might also be due, at least in part, to steric hindrance to attack at the central carbon owing to the proximate cyclopropane methyl functions, and because of ground-state steric strain arising from the nonbonded interactions in **1**.[8]

Pasto, Chen, and Binsch have provided a theoretical basis for the differences in reactivity of alkenylidene- and methylenecyclopropanes in cycloaddition reactions,[10] and for the stability of cations such as **2**, based on an interaction of the C_4–C_5 π bond of an alkenylidene cyclopropane, or the in-plane p orbital on C_4 in **2**, with the appropriate Walsh orbitals of the cyclopropane moiety.[11]

The motivations for the present research were, in effect, twofold. It was anticipated that reactions of alkenylidenecyclopropanes of differing electronic, steric, and stereochemical features with chlorosulfonyl isocyanate (CSI) would provide product distributions from which information relating to mechanisms and the stability of intermediates would be available. Secondly, it was desired to investigate cycloaddition reactions of alkenylidene-, methylene-, and vinylcyclopropanes[12] proceeding *via* two-step, dipolar intermediate reactions for comparison with the reactivity and mode of reaction of these systems with 4-phenyl-1,2,4-triazoline-3,5-dione.[10,11] The choice of CSI[13] as the electrophilic reagent for use in these studies was based on past observations from one of these laboratories, which have demonstrated a number of discrete advantages which occur from the utilization of this uniparticulate electrophile[14] for the investigation of electrophilic additions.[15] In the present context, this type of reagent was anticipated to be an unusually effective probe for the elucidation of competitive rate situations surrounding the intramolecular capture of various transient carbonium ions.

Recent studies by Moriconi and Kelly[16] attest to the fact that the principal mode of CSI addition to a variety of allenes occurs at the central carbon to produce *N*-chlorosulfonyl-β-lactams such as **4**. Under similar conditions, **1** reacts with CSI to produce only **5**, in which the electropositive center of CSI has become attached to the terminal allenic carbon.[8] Consequently, the disparity in chemical behavior noted earlier for the protonation of **1** and **3** is carried over without apparent discrepancies into uniparticulate additions.



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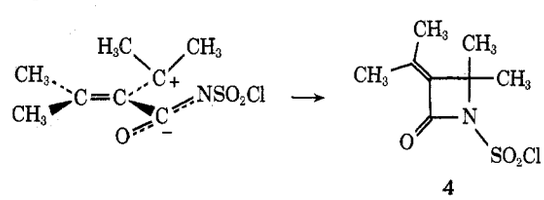

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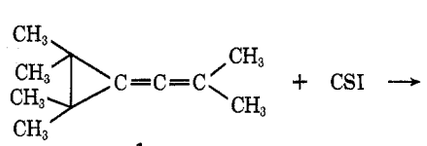
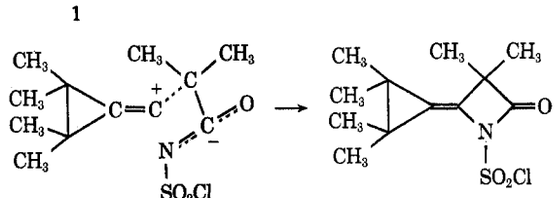


1



5

Results

2-Phenylisobutenylidenecyclopropane (6) with CSI. —The reaction of **6** with CSI produced a mixture of adducts (see Scheme I) as indicated by analysis of the nmr and ir spectra of the reaction product. Direct chromatographic separation of the CSI adducts on

(5) K. Griesbaum, *Angew. Chem., Int. Ed. Engl.*, **5**, 933 (1966); **8**, 933 (1969).

(6) J.-P. Bianchini and A. Guillemonat, *Bull. Soc. Chim. Fr.*, 2120 (1968).

(7) J. K. Crandall, D. R. Paulson, and C. A. Bunnell, *Tetrahedron Lett.*, 5063 (1968).

(8) M. L. Poutsma and P. A. Ibarbia, *J. Amer. Chem. Soc.*, **93**, 404 (1971).

(9) For current views on this topic see M. Hanack and H.-J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6**, 666 (1967); G. A. Olah, D. P. Kelley, C. L. Jeuell, and R. D. Porter, *J. Amer. Chem. Soc.*, **92**, 2544 (1970).

(10) D. J. Pasto and A. F.-T. Chen, *ibid.*, **93**, 2562 (1971); *Tetrahedron Lett.*, 2995 (1972).

(11) See reference in footnote 1a.

(12) D. J. Pasto and A. F.-T. Chen, *Tetrahedron Lett.*, in press.

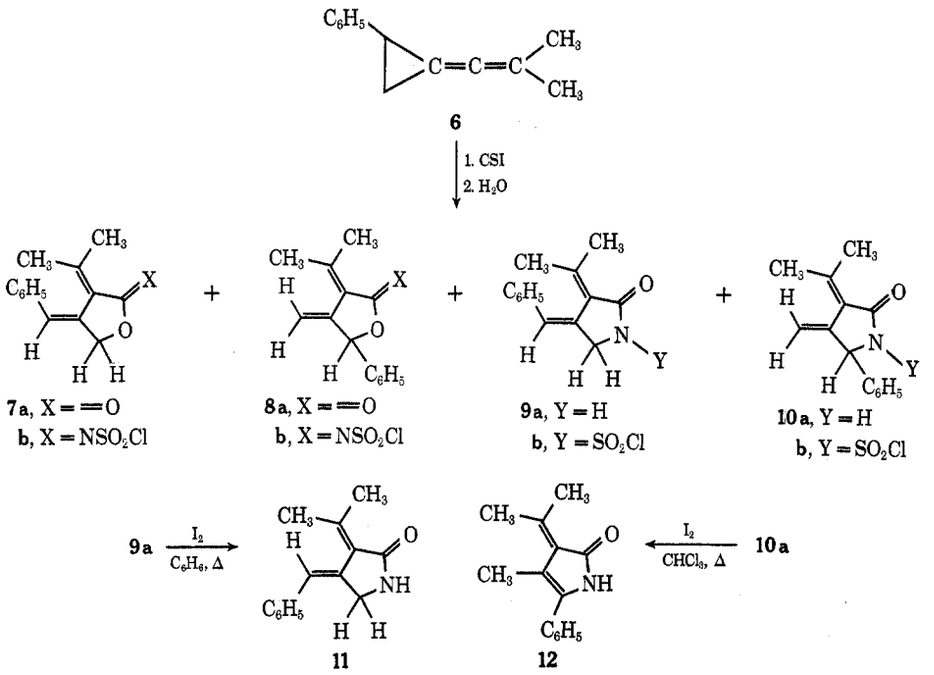
(13) R. Graf, *Chem. Ber.*, **89**, 1071 (1956).

(14) As previously defined,[15a] these reagents are those which are incapable of fragmentation during the course of bonding to an electron-rich system.

(15) For leading references, see (a) ref 1b; (b) L. A. Paquette, J. R. Allen, Jr., and M. J. Broadhurst, *J. Amer. Chem. Soc.*, **93**, 4503 (1971); (c) L. A. Paquette, M. J. Broadhurst, C. Lee, and J. Clardy, *ibid.*, **94**, 630 (1972).

(16) E. J. Moriconi and J. F. Kelly, *J. Org. Chem.*, **33**, 3036 (1968).

SCHEME I



silica gel resulted in the isolation of pure fractions of adducts **7b–10b**. The structures of the adducts have been assigned on the basis of high-resolution mass spectral *m/e* measurements and ir and nmr spectral properties, and by identification of their hydrolysis products.

N-Chlorosulfonylimino ether **7b** displays characteristic absorption bands in the ir at 1640 ($\nu_{C=C}$), 1575 ($\nu_{C=N}$), and 1372 and 1172 cm^{-1} (ν_{SO_2}). The nmr spectrum of **7b** exhibits methyl singlets at δ 1.54 and 2.33, a doublet at 5.10 (J = 2.0 Hz), for the methylene hydrogens, and a triplet at 6.58 (J = 2.0 Hz, vinyl hydrogen), with the aromatic hydrogens appearing at 7.25. The high-field methyl resonance of **7b** is characteristic of the "inside" methyl of the isopropylidene function positioned directly over the face of the phenyl ring which is twisted perpendicularly to the plane of the diene chromophore.[17,18] Hydrolysis of **7b** produced lactone **7a**, identified by high-resolution mass spectral *m/e* measurements and the ir ($\nu_{C=O}$ at 1750 cm^{-1}) and nmr spectral properties. The nmr spectrum, for example, again displays the characteristic high-field methyl resonance at δ 1.47 (see Table I for the remainder of the spectrum).

The *N*-chlorosulfonylimino ether **8b** possesses ir spectral properties very similar to those of **7b**, the structural identification being based on the very definitive resonance patterns appearing in the nmr spectrum of **8b**. Hydrolysis of **8b** produced a lactone (**8a**) which possesses spectral properties commensurate with the proposed structure.

The *N*-chlorosulfonyl-γ-lactam **9b** was similarly identified by its chemical and physical properties. The ir spectrum of **9b** contains a carbonyl band at 1748 cm^{-1} along with the typical ν_{SO_2} bands at 1420 and 1197 cm^{-1}. The nmr spectrum of **9b** is very similar to that of **7b** (see Table I), clearly indicating the presence of the "inside" methyl and phenyl functions of **9b**. Hydrolysis of **9b** produces lactam **9a**, the nmr spectrum of which contains the high-field methyl resonance. Treatment of lactam **9a** with a catalytic quantity of iodine in refluxing benzene resulted in quantitative isomerization to **11**. The high-field methyl resonance of **9a** has shifted downfield to δ 2.22 in **11**, while the hydrogen of the benzylidene group has shifted 0.20 ppm to lower field owing to long-range deshielding by the isopropylidene double bond and the methyl group (see Table I for the nmr data for **11**). The quantitative isomerization of **9a** to **11** is dramatic evidence that this lactam suffers internal steric effects which are relieved on isomerization of the phenyl from the "inside" to the "outside" of the diene chromophore.

Adduct **10b** possesses ir spectral properties very similar to those of **9b**, and nmr chemical shifts very similar to those of **8b** (see Table I). Hydrolysis of **10b** produces a lactam (**10a**) which, on treatment with iodine in deuteriochloroform, underwent allylic rearrangement to lactam **12**. Migration of the double bond during the isomerization of **10a** to **12** was most clearly evidenced by the large bathochromic shift in the uv absorption spectra [$\lambda_{max}^{95\%\ C_2H_5OH}$ 263.5 nm (ϵ 10,100) for **10a** to 372.5 (5180) in **12**], and the appearance of a third sp^2 C-bound methyl resonance in the nmr spectrum.

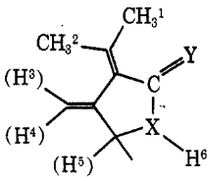
The assignment of nmr chemical shifts to the appropriate hydrogens in adducts **7b–10b** allows for the direct determination of the yields of **7b–10b** by integration of the aromatic hydrogen and δ 4–7 regions of the nmr spectrum of the crude reaction mixtures. Integration of the aromatic and δ 4–7 regions gives a ratio of 5.0:3.0, indicating that **7b–10b** are the only products formed (all resonances appearing in the nmr spectrum of the crude reaction mixture have been assigned as belonging to **7b–10b**), and that they are formed in essentially quanti-

(17) Similar shielding of the "inside" methyl by an "inside" phenyl has been observed in the adducts of phenyl-substituted alkenylidenecyclopropanes with 4-phenyl-1,2,4-triazoline-3,5-dione.[1a,10]

(18) Additional evidence that the phenyl ring of adducts such as **7b** is twisted out of the plane of the diene chromophore is provided by the uv absorption data of compounds possessing the stereochemistry present in **7b** and compounds in which the phenyl resides "outside" of the diene chromophore, the isomerization of the phenyl from the "inside" to the "outside" resulting in a substantial bathochromic shift (*vide infra*; see also ref 1a and 10).

TABLE I

NMR PARAMETERS FOR **7a–10a, 7b–10b,** AND **11** (δ)



Compd	H¹	H²	H³	H⁴	H⁵	H⁶	Aromatic H
7a	2.30	1.47		6.44	4.77 (d, J = 2.0 Hz)		7.27
8a	2.52	2.17	5.32	4.98	5.66		7.27
9a	2.28	1.37		6.50 (t, J = 1.8 Hz)	3.98 (d, J = 1.8 Hz)	7.0	7.25
10a	2.54	2.10	5.04	4.97	5.30	6.15	7.25
7b	2.33	1.54		6.58 (t, J = 2.0 Hz)	5.10 (d, J = 2.0 Hz)		7.25
8b	2.56	2.28	5.45	5.10	6.09		7.32
9b	2.32	1.47		6.61	4.48		7.25
10b	2.54	2.17	5.37	5.11	5.50		7.30
11	2.47	2.22	6.72		4.22 (d, J = 2.1 Hz)	*a*	7.25

[a] Could not be unambiguously assigned.

tative yield. The ratios of the products (**7b–10b**) formed at −30 and 38° were measured by carrying out the reaction in the nmr probe. The product ratios remain constant with time at both temperatures, and are given in Table II.

TABLE II

YIELDS OF ADDUCTS **7b–10b** FROM **6** WITH CSI

7b	8b	9b	10b	Temp, °C
9	15	43	33	−30
19	17	33	31	38

***trans*-2-Methyl-3-phenylisobutenylidenecyclopropane (13) with CSI.**—The ir spectrum of the crude product obtained from the reaction of **13** with CSI (Scheme II) indicated the presence of *N*-chlorosulfonylimino ether ($\nu_{C=N}$ 1570–1590 cm^{-1}) and *N*-chlorosulfonyl-γ-lactam ($\nu_{C=O}$ 1750 cm^{-1}) functions, and a major product(s) with $\nu_{C=O}$ 1788 cm^{-1} identified as belonging to a *N*-chlorosulfonyl-β-lactam (*vide infra*). The nmr spectrum of the product mixture similarly indicated the formation of a complex mixture of products. Furthermore, integration of the aromatic and δ 4–7 regions indicated that the major product(s) did not contain vinyl or other low-field hydrogens.

Chromatographic separation of the CSI adduct mixture provided a fraction with $\nu_{C=O}$ 1788 cm^{-1}. The nmr spectrum of this fraction indicated the presence of two isomeric compounds in an approximate 90:10 ratio, the principal component giving rise to methyl singlets at δ 1.15 and 1.47, a methyl doublet at 1.42, a double quartet at 1.97 (1 H), and a doublet at 2.41 (1 H) with the aromatic hydrogen resonances appearing at 7.14. Ozonolysis in dichloromethane–pyridine did not produce acetone, thus eliminating the possible presence of an isopropylidene function. The physical and chemical data are consistent with either structure **14** or **15** as the major component of this fraction. We tentatively assign structure **14** as the principal component based on the presence of a high-field methyl resonance arising from long-range shielding by the syn phenyl. Acid hydrolysis of the mixture of **14** and **15** produces an ~1:1 mixture of the ketones **16** and **17** ($\nu_{C=O}$ 1694 cm^{-1}, cyclopropyl ketone). The mass spectrum of the mixture of **16** and **17** clearly established the gross structure of the ketones as $C_{10}H_{11}CO_2C_3H_7$ (see Experimental Section). The nmr spectrum is entirely consistent with the assigned structures.

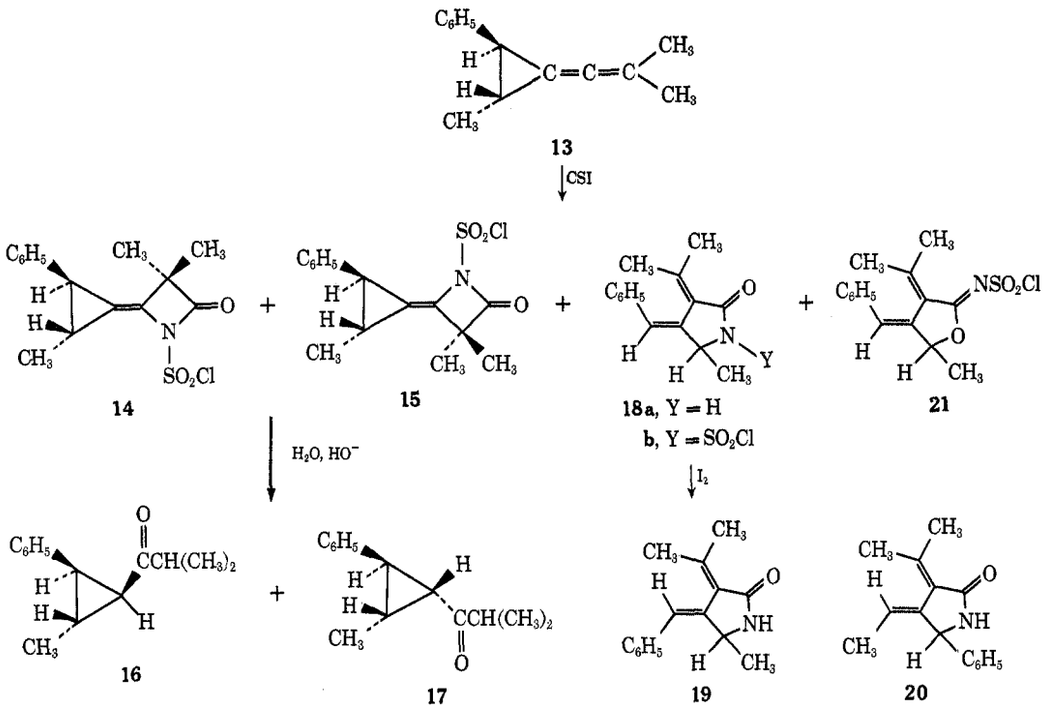
Also isolated from the initial reaction mixture were pure fractions of **18b** and **21**. Both adducts gave ir and nmr spectra fully consistent with the proposed structures.

Hydrolysis of the CSI adduct mixture followed by chromatographic separation led to the isolation of a mixture of ketones **16** and **17**, lactam **18a**, a mixture of lactams **18a** and **19**, and a small amount of lactam **20**. Identification of the structure of lactam **18a** is based on the presence of a high-field methyl resonance in the nmr spectrum, and the quantitative isomerization of **18a** to **19** by iodine in deuteriochloroform. The identification of lactam **19** in the mixture of **18a** and **19** is based on a comparison of the nmr spectral properties of **19** in the mixture with those of pure **19** obtained by isomerization of **18a**. The structure of lactam **20** is based on a comparison of the nmr spectral properties of **20** with those of lactam **25** isolated from the reaction of **22** with CSI (see Scheme III). In particular, the ethylidene hydrogen appears at lower field in **20** consistent with its being "inside" the diene chromophore, and the $CH_3CH=$ resonance appears at higher field owing to shielding by the phenyl.

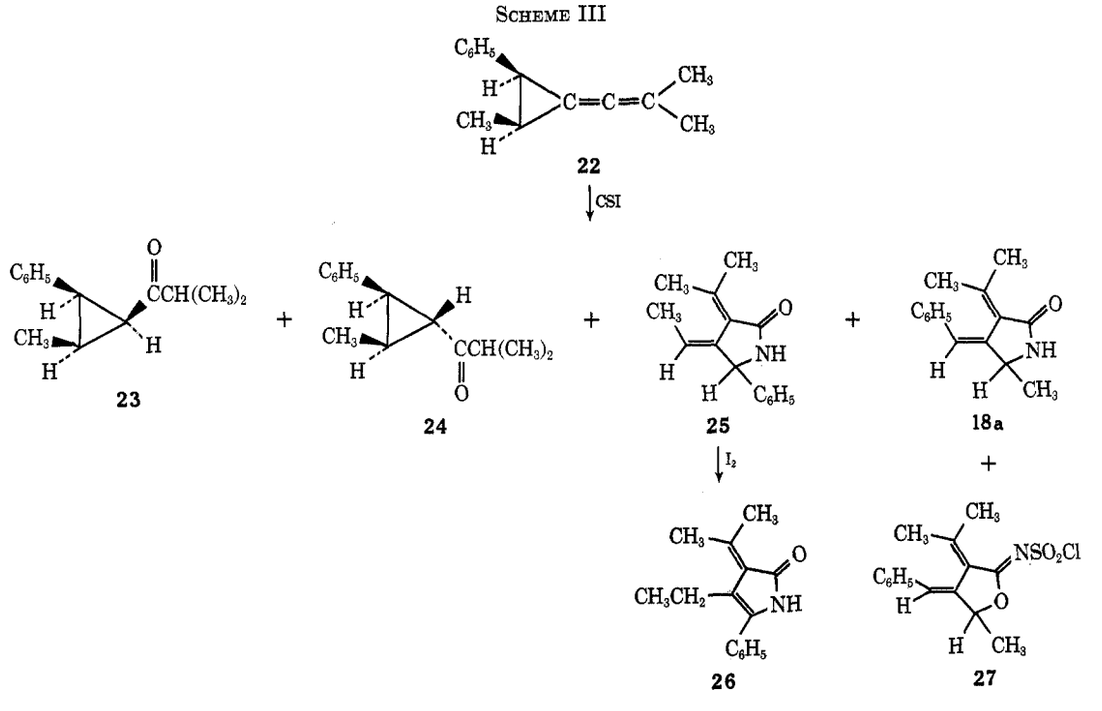
***cis*-2-Methyl-3-phenylisobutenylidenecyclopropane (22) with CSI.**—The ir spectrum of the reaction mixture displayed intense absorption at 1778 cm^{-1} (*N*-chlorosulfonyl-β-lactam) along with very weak bands at 1751 and 1580 cm^{-1} (*N*-chlorosulfonyl-γ-lactam and *N*-chlorosulfonylimino ether, respectively). The nmr spectrum indicated that cyclopropane ring-opened products were formed in less than 20% yield.

Hydrolysis of the reaction mixture followed by chromatographic separation gave as the major fraction a mixture of the ketones **23** and **24** which were identified from ir, nmr, and mass spectral data (see Experimental Section). The major ring-opened product was identified as **25** on the basis of elemental analysis and comparison of nmr chemical shift data with that of **20** derived from **13** with CSI. Lactam **25** undergoes isomerization in the presence of iodine in deuteriochloroform to produce

SCHEME II



SCHEME III



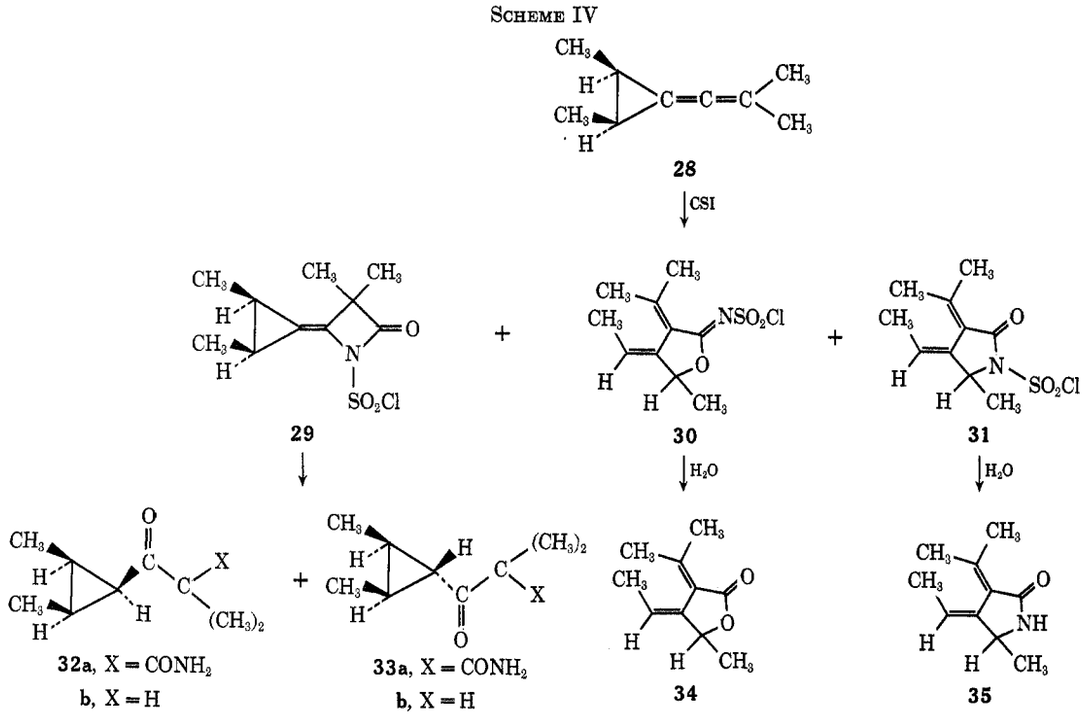
lactam **26**, the nmr spectrum of which displays very characteristic $CH_3CH_2C=$ resonances. A small quantity of lactam **18a** was also isolated, as well as a small quantity of the imino ether **27**. (The *N*-chlorosulfonylimino ethers hydrolyze rather slowly and sometimes survive the hydrolysis procedure. The lactone corresponding to **27** was not isolated.)

***cis*-2,3-Dimethylisobutenylidenecyclopropane (28) with CSI.**—The nmr spectrum of the product mixture indicated the formation of a moderate quantity of cyclopropane ring-opened product(s) (Scheme IV). Direct chromatographic separation gave pure fractions of the *N*-chlorosulfonyl-β-lactam **29** (51%, $\nu_{C=O}$ 1793 cm^{-1}), *N*-chlorosulfonylimino ether **30** (8.5%, $\nu_{C=N}$ 1575 cm^{-1}), and the *N*-chlorosulfonyl-γ-lactam **31** (15.5%, $\nu_{C=O}$ 1748 cm^{-1}).

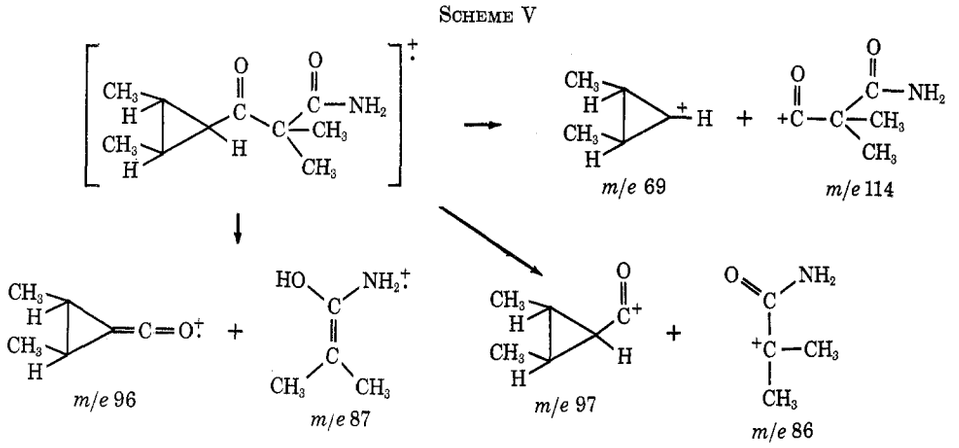
Basic hydrolysis of **29** produced a mixture of keto amides **32a** and **33a**, whereas acid hydrolysis produced a mixture of the ketones **32b** and **33b**.[19] The structures of the keto amides are clearly indicated by ir ($\nu_{C=O}$ 1691

(19) It is interesting to note the distinctly different behavior of the *N*-chlorosulfonyl-β-lactams toward acid- and base-catalyzed hydrolysis. The keto amides are stable under the conditions used for the acid-catalyzed hydrolyses of the *N*-chlorosulfonyl-β-lactams. It is clearly evident that the acid- and the base-catalyzed reactions proceed by grossly different mechanisms, the former proceeding *via* an enamino acid involving cleavage of the N–C=O bond, while the latter involves cleavage of the vinyl C–N bond.

SCHEME IV



SCHEME V



and 1672 cm^{-1}, ν_{NH_2} 3502 and 3398 cm^{-1}), nmr (see Experimental Section), and mass spectra. The mass spectrum of the mixture of **32a** and **33a** clearly indicated the gross structure $C_5H_9CO_2C(CH_3)_2CONH_2$ by the presence of appropriate fragment and metastable peaks (see Scheme V).

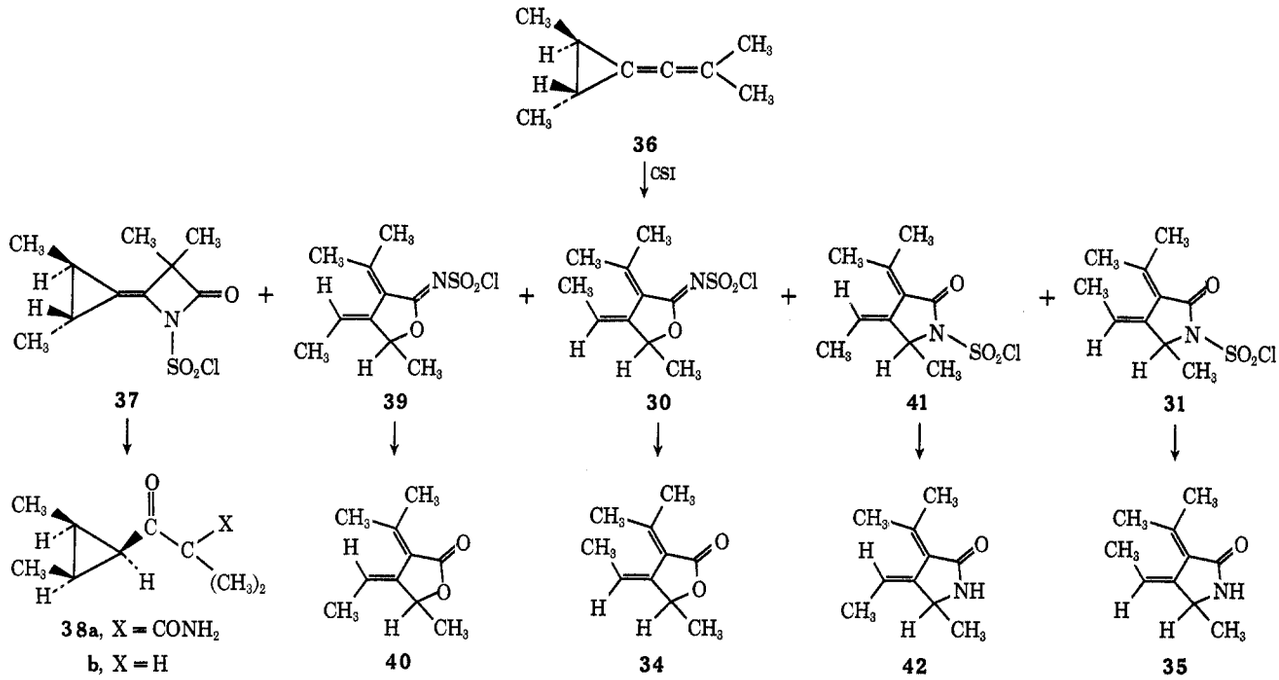
The structures of the ketones **32b** and **33b** were clearly indicated by the ir (1685 cm^{-1}) and mass spectra (see Experimental Section) of the mixture.

Hydrolysis of **30** and **31** produced the lactone **34** and lactam **35**, respectively. The stereochemistry about the ethylidene function was assigned by comparison of the nmr spectra of **34** and **35** with the spectra of the mixtures of lactones and lactams derived from **36**, the ethylidene vinyl hydrogens of **34** and **35** appearing at higher field than the "inside" hydrogens of **40** and **42** (see Scheme VI) as pointed out earlier.

trans-**2,3-Dimethylisobutenylidenecyclopropane (36) with CSI.**—Alkenylidenecyclopropane **36** reacts with CSI to give as the major product a *N*-chlorosulfonyl-β-lactam (~90% by ir and nmr analysis of the reaction product mixture). Chromatographic separation of the reaction mixture gave pure *N*-chlorosulfonyl-β-lactam **37**, and small quantities of a 3:1 mixture of the *N*-chlorosulfonylimino ethers **30** and **39** (6%, $\nu_{C=N}$ 1568 cm^{-1}) and a 4:1 mixture of the *N*-chlorosulfonyl-γ-lactams **31** and **41** (2%, $\nu_{C=O}$ 1743 cm^{-1}).

The structures of the adducts were assigned on the basis of their hydrolysis products. Basic hydrolysis of **37** produced a single, crystalline keto amide **38a** easily identified by its ir, nmr, and mass spectra (see Experimental Section), while acid hydrolysis produced a single ketone **38b**. Hydrolysis of the mixture of **30** and **39** produced a mixture of lactones, the major isomer possessing nmr chemical shifts identical with those of **34** derived from **28**. The ethylidene vinyl hydrogen of the minor isomer (**40**) appears at lower field than its counterpart in **34**, indicating the stereochemistry as shown in **40**. Similarly, hydrolysis of the mixture of **31** and **41** produced a mixture of lactams, the major isomer (**35**) being identical with the lactam derived from **28**. The stereochemistry about the ethylidene functions in the two amides was assigned as described for the lactones (see Experimental Section for details of the nmr spectra).

SCHEME VI



Discussion

Electrophilic attack by CSI on the alkenylidenecyclopropane can occur either at C_1, C_4, or C_5. Competition between these modes of reaction is expected to be sensitive to steric effects engendered by substituents on the alkenylidenecyclopropane with the approaching CSI, steric effects in the resulting dipolar intermediates, and stabilization afforded the cationic center. The factors affecting the stereochemistry about the benzylidene or ethylidene functions in the cyclopropane ring-opened products arise not only in the initial step of the reaction, but also in the second step, during which the dipolar intermediates collapse to products.

Although electrophilic attack at C_1 would be expected to be favorable owing to a decrease in bond-angle strain about C_1, it is expected to be less so than the other two modes because of steric hindrance to CSI approach by the substituents attached to the cyclopropane moiety, and because of less stabilization afforded the cationic center in the dipolar intermediate **43** (Scheme VII).

Bonding by CSI at C_5 results in the formation of the dipolar intermediate **44**. The vacant orbital thus formed on C_4 is perfectly aligned for interaction with the Walsh orbitals[20] of the cyclopropane ring similar to the interaction between the C_4–C_5 π system and the cyclopropane ring in the starting alkenylidenecyclopropane as discussed in an earlier article.[1a] The cationic portion of the dipolar intermediate may thus be compared in a limited sense to an allyl cation, for which the resonance structures illustrated in Figure 1 may be written. (The molecular orbital representation of the resulting hybrid is illustrated below the resonance contributing structures in Figure 1.) Alkyl and aryl substituents bonded to the cyclopropane ring should lend inductive and resonance stabilization, respectively, to the delocalized cation (akin to the well-known stabilization of allyl cations by alkyl and aryl functions).

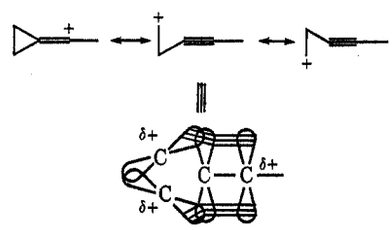


Figure 1.—Resonance structures and MO description of the cyclopropylmethylene cation.

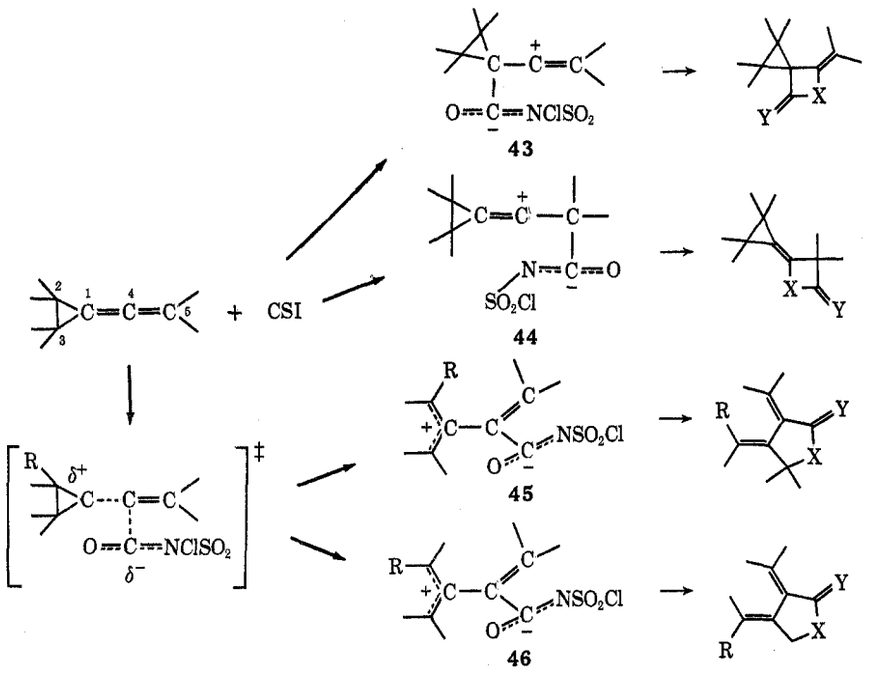
Electrophilic attack by CSI at C_4 can lead either to the development of a cyclopropyl cation, which is expected to undergo concerted disrotatory ring opening to produce a resonance-stabilized allylic cation,[21,22] or a nonresonance-stabilized tertiary cation at C_5. The former mode of reaction would appear to be quite favorable owing to the release of the strain energy of the three-membered ring and the stabilization of the incipient allylic cation. In this mode of reaction there are, in fact, two different pathways of disrotatory ring opening, one leading to **45** in which adverse steric effects are absent and the other leading to **46** in which severe steric interactions arise owing to the R function which is forced to reside "inside" the cavity of the allylic cation. In the present work, only the former mode of disrotatory ring opening is observed (except in the case of the trans 2,3-disubstituted alkenylidenecyclopropane in which one of the substituents must be placed in the "inside" of the allylic cation). Bonding by CSI at C_4 will suffer steric deceleration by functions attached to the cyclopropane ring which impede the approach of CSI to C_4, or which force a function to reside on the "inside" of the allylic

(20) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(21) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

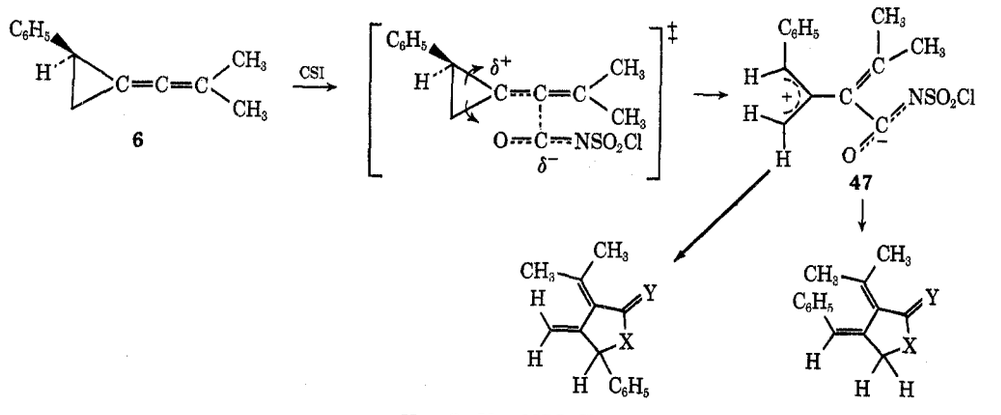
(22) For leading references see (a) P. v. R. Schleyer, W. F. Sliwinski, G. W. Van Dine, U. Schöllkopf, J. Paust, and K. Fellenberger, *J. Amer. Chem. Soc.*, **94**, 125 (1972); (b) W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *ibid.*, **94**, 133 (1972), and references contained in ref 22a.

SCHEME VII



X = O; Y = NSO_2Cl
Y = O; X = NSO_2Cl

SCHEME VIII



X = O; Y = NSO_2Cl
X = NSO_2Cl; Y = O

cation in the dipolar intermediate. Of the three possible modes of reaction of an electrophile (CSI) with an alkenylidenecyclopropane, only those occurring at C_4 (with generation of cyclopropyl cation character at C_1 and concomitant disrotatory ring opening) and C_5 are observed. The results of the present study reveal that the competition between these two modes is a sensitive function of the type, number, and stereochemical relationship of substituents attached to the cyclopropane ring.

Alkenylidenecyclopropane **6** suffers electrophilic attack by CSI only at C_4, resulting in the formation of cyclopropane ring-opened products. With **9** steric factors are minimal, and stabilization of the ring-opened allylic cation is maximal. Of two disrotatory modes of ring opening, only that producing the more stable allylic cation in **47** is observed (see Scheme VIII). Collapse of the dipolar intermediate to products occurs to an essentially equal extent at both ends of the allylic cation, C–N bond formation being slightly favored over C–O bond formation.

In contrast to the reaction of **6** with CSI, **13** and **22** suffer extensive electrophilic attack at C_5, leading to the formation of *N*-chlorosulfonyl-β-lactams. One might have anticipated that both steric hindrance to attack by CSI at C_4 and adverse steric effects generated in the disrotatory ring-opening process would disfavor attack at C_4 of **13**.[22] These steric interactions, however, are not present in the case of the reaction of the cis isomer **22** with CSI (approach trans to the phenyl and methyl functions is not sterically impeded compared to the case of **6**), which, nonetheless, undergoes extensive, albeit somewhat less, electrophilic attack at C_5.[23] The domi-

(23) A similar reduction in reactivity toward cyclopropane ring-opening reactions of cis- and trans-substituted cyclopropyl cations has been reported by Parham and Yong,[24] in which the silver ion assisted solvolysis of *cis*-2,3-di-*n*-propyl-1,1-dichlorocyclopropane occurs 24 times faster than with the *trans*-2,3-di-*n*-propyl isomer.

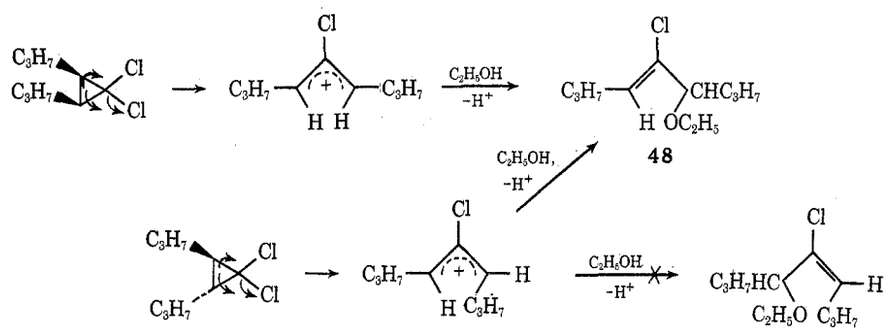
(24) W. E. Parham and K. S. Yong, *J. Org. Chem.*, **33**, 3947 (1968).

nant factor leading to more extensive attack at C_5 must be the stabilization of the intermediate cation (similar to **44** in Scheme VII) by the methyl group attached to the cyclopropane ring. Further evidence in support of this proposal is provided by the results derived with the 2,3-dimethylalkenylidenecyclopropanes **28** and **36**, both of which undergo even more extensive attack at C_5, and the results reported by Poutsma and Ibarbia[3] for **1** which produces exclusively **5**.

A closer analysis of the products derived from the cyclopropane ring-opened dipolar intermediates from **13** and **36** indicates that collapse of the dipolar intermediates occurs predominantly at the allylic carbon bearing the function constrained to the "inside" of the allylic cation structure.[25] This is consistent with the results of Parham and Yong[24] reported for the solvolysis of *cis*- and *trans*-2,3-di-*n*-propyl-1,1-dichlorocyclopropane, in which both substrates produce only (*Z*)-5-chloro-6-ethoxy-4-nonene (**48**). This behavior must be the result of a sterically enforced distortion of the allylic cation system resulting in a decrease in the stabilization of the positive charge afforded by the proximate double bond, thus inducing greater reactivity toward C–O and C–N bond formation at that carbon. Based on this rationale, it is possible to infer the structure of the dipolar intermediate derived from **13** with CSI from the structures of the cyclopropane ring-opened products. Collapse of intermediate **49** (see Scheme IX) produces **50** and **51**, which correspond in structure to adducts **18a** and **20**, and **21**. Collapse of intermediate **52** would be expected to give rise to **53** and **54**, neither of which are formed. This evidence strongly suggests that the only dipolar intermediate formed in the reaction of **13** and CSI is **49**. The greater stability, and thus preferential formation, of **49** must be due to the presence of the styrene chromophore in the twisted allylic cation portion of **49**.

A further aspect concerning the stereochemistry of the benzylidene and ethylidene functions merits comment. The isomers with phenyl or methyl residing "inside" the diene chromophore are the least thermodynamically stable. Although the stereochemistry of the final product is determined in the cyclopropane ring-opening step, the thermodynamic instability inherent in the product, however, does not arise in the first step, but arises in the subsequent collapse of the dipolar intermediates to the final products. The structure of the dipolar intermediates as initially formed is that illustrated in **55** of Scheme X in which there is very little steric interaction between the R and the subsequent "inside" methyl of the isopropylidene function (the rotational processes occurring in the collapse of **55** are indicated by arrows).

The relative amounts of C–O and C–N bond formation in the collapse of the dipolar intermediates varies with temperature (see Table II), the structure of the alkenylidenecyclopropane, and the structure of the product.[27] In the present studies the four-membered ring products are formed exclusively by C–N bond formation, while the five-membered ring products are formed by both C–N and C–O (the former dominating) bond formation. No trend in the preference for C–N *vs.* C–O bond formation is readily apparent.



Experimental Section

Melting points are corrected. Proton magnetic resonance spectra were obtained with Varian A-60A and XL-100 spectrometers. The reported coupling constants are derived by first-order analyses of the nmr spectra. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. High-resolution mass measurements and mass spectra were recorded on a Picker Nuclear MS-902 spectrometer.

Preparation of Alkenylidenecyclopropanes.—The procedure of Hartzler[31] was used to prepare the alkenylidenecyclopropanes[1a] by the addition of 3,3-dimethylallene carbene to the requisite alkene.

Reactions of Alkenylidenecyclopropanes with CSI. Procedure A.—To a solution of 0.01 mol of the alkenylidenecyclopropane in 15 ml of dichloromethane at −78° under a nitrogen atmosphere was added 0.01 mol of CSI in 10 ml of dichloromethane. After 5 hr at −78° the reaction mixtures were poured into 100 ml of water and shaken for 30 min. The organic layers were separated, dried, and evaporated, and the residues were chromatographed on Florisil.

Procedure B.—To a solution of the alkenylidenecyclopropane in dichloromethane (0.3 *M*) maintained at 0° was added a solution of CSI in dichloromethane (0.3 *M*). The reaction mixtures were allowed to warm to room temperature and stirred for 30 min. The solvent was then removed on a rotatory evaporator, and the ir and nmr spectra were immediately recorded. The

(25) The possible isomerization of allylic cations does not occur, as evidenced by the lack of isomerization crossover products from **22** and **28**, and the fact that the isomerization of allylic cations requires activation energies in excess of 15 kcal/mol,[26] which indicates that collapse of the dipolar intermediate must occur more rapidly than isomerization.

(26) P. v. R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 5174 (1969).

(27) Differences in the preference for C–N *vs.* C–O bond formation as a function of structure has been noted previously in the reactions of cyclooctatetraene,[28] cycloheptatriene,[29] and bullvalene.[30]

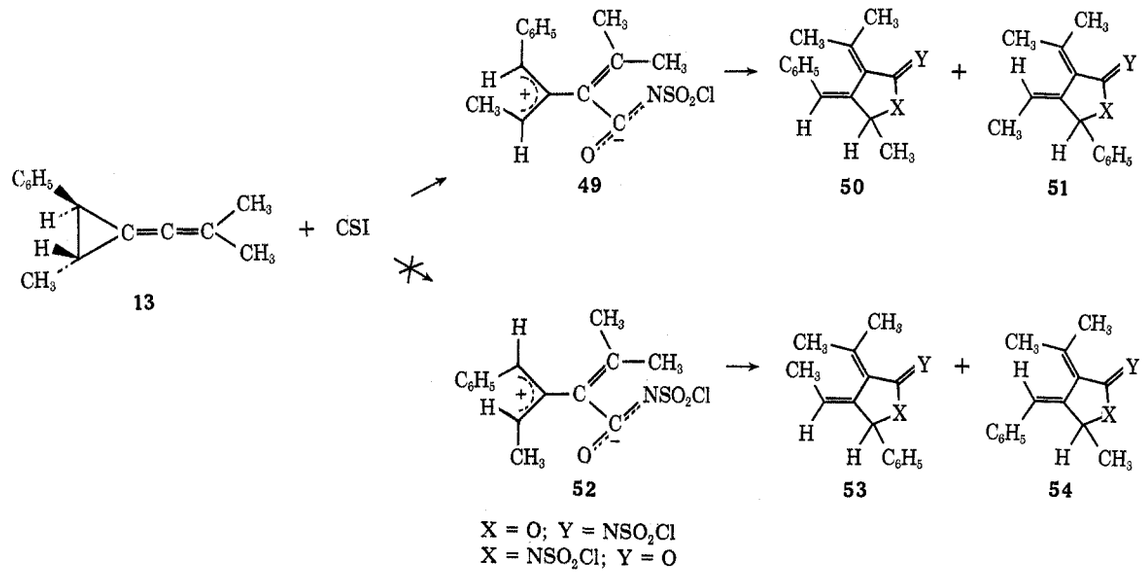
(28) L. A. Paquette, J. R. Malpass, and T. J. Barton, *J. Amer. Chem. Soc.*, **91**, 4714 (1969); L. A. Paquette and T. J. Barton, *ibid.*, **89**, 5480 (1967).

(29) E. J. Moriconi, C. F. Hummel, and J. F. Kelly, *Tetrahedron Lett.*, 5325 (1969).

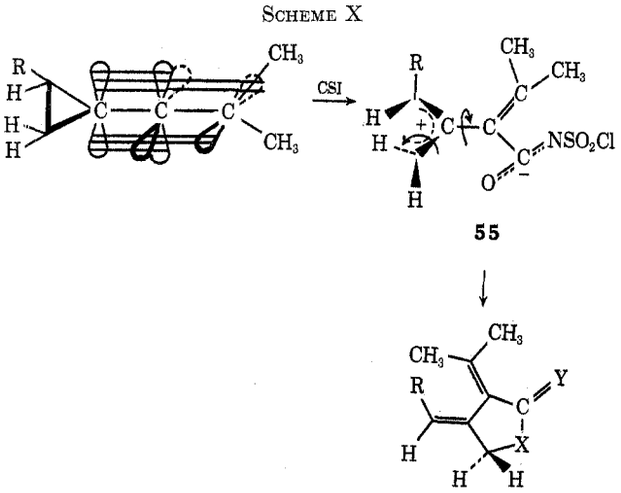
(30) L. A. Paquette, S. Kirschner, and J. R. Malpass, *J. Amer. Chem. Soc.*, **91**, 3970 (1969); **92**, 4330 (1970).

(31) H. D. Hartzler, *ibid.*, **83**, 4990 (1961).

SCHEME IX



SCHEME X



reaction mixtures were either separated directly by chromatography, or were hydrolyzed and then separated as described in the following paragraphs.

Separation of the CSI adducts was accomplished by column chromatography on silica gel.[32] Elution with hexane afforded the *N*-chlorosulfonyl-β-lactams, while elution with ~5% ether–hexane furnished separate fractions of the *N*-chlorosulfonyl-γ-lactams, and elution with ~10% ether–hexane afforded separate fractions of the *N*-chlorosulfonylimino ethers. The CSI adducts were further purified by recrystallization from ether.

The CSI adducts were hydrolyzed by dissolution in 20% aqueous acetone maintaining a pH of ~7–8 by titration with 0.2 *M* potassium hydroxide. After the hydrolyses were complete, the reaction mixtures were extracted with dichloromethane. The organic layers were dried ($MgSO_4$ for lactones, K_2CO_3 for lactams) and the solvent was removed under reduced pressure.

Reaction Products of 6 with CSI. Adduct 9b (30.5% isolated yield) had mp 115.0–115.5°; ir ($CHCl_3$) 1750 (C=O), 1608 (C=C), 1409 and 1189 cm^{-1} (SO_2); nmr, see Table I; mass spectrum (70 eV) *m/e* (calcd for $C_{14}H_{14}{}^{35}ClNO_3S$, 311.039) 311.042.

Adduct 10b (26.4%) had mp 108–110°; ir ($CHCl_3$) 1750 (C=O), 1630 (C=C), 1404, and 1196 cm^{-1} (SO_2); nmr, see Table I.

Adduct 7b (17%) was not obtained crystalline: ir ($CHCl_3$) 1613 (C=C), 1577 (C=N), 1367, and 1164 cm^{-1} (SO_2); nmr, see Table I.

Adduct 8b (19%) had mp 93–95°; ir ($CHCl_3$) 1613 (C=C), 1568 (C=N), 1370, and 1162 cm^{-1} (SO_2); nmr, see Table I.

Lactam 9a had mp 166–167.5°[33] (from ether); ir 3440 (NH), 1690 (C=O), 1635 (amide II), and 1627 cm^{-1} (C=C); uv max (95% ethanol) 297.5 nm (ε 7220); nmr, see Table I; mass spectrum *m/e* (calcd for $C_{14}H_{15}NO$, 213.116) 213.115.

Lactam 10a had mp 167–168°[33] (from ether); ir 3441 (NH), 1690 (C=O), and 1630 cm^{-1} (amide II or C=C); uv max (95% ethanol) 263.5 nm (ε 10,000); nmr, see Table I; mass spectrum *m/e* (calcd for $C_{14}H_{15}NO$, 213.116) 213.116.

Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.67; H, 7.09; N, 6.70.

Lactone 7a was a viscous liquid: ir 1750 (C=O) and 1622 cm^{-1} (C=C); nmr, see Table I; mass spectrum *m/e* (calcd for $C_{14}H_{14}O_2$, 214.099) 214.097.

Lactone 8a was a viscous liquid: ir 1747 (C=O) and 1630 cm^{-1} (C=C); nmr, see Table I; mass spectrum *m/e* (calcd for $C_{14}H_{14}O_2$, 214.099) 214.099.

Isomerization of 9a to 11.—A solution of 120 mg of **9a** and 5 mg of iodine in 1.5 ml of benzene in a sealed ampoule was heated at 70–80° for 24 hr. The reaction mixture was directly chromatographed on silica gel, giving **11** on elution with 50% benzene–hexane: mp 199–202° dec; ir 3440 (NH), 1690 (C=O), and 1627 cm^{-1} (amide II and C=C); nmr, see Table I; mass spectrum *m/e* (calcd for $C_{14}H_{15}NO$, 213.116) 213.113.

Isomerization of 10a to 12.—Into an nmr tube were introduced approximately 40 mg of **10a**, an appropriate volume of deuteriochloroform, and a few crystals of iodine. The tube was sealed and heated at 70° for 3 hr, at which time the conversion to **12** was seen to be complete. Chloroform was added, and the solution was washed with aqueous sodium thiosulfate, dried, and evaporated. Recrystallization of the solid from acetone gave **12** as yellow crystals: mp 202–203°; ir 1682 cm^{-1} (C=O); uv max (95% ethanol) 372.5 nm (ε 5180); nmr ($CDCl_3$) δ 2.19, 2.28, 2.48 (s, 3 H each, $-CH_3$'s) and 7.40 (s, 5 H, aromatic H).

Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.78; H, 6.82; N, 6.64.

Reaction Products Derived from 13 with CSI. Mixture of adducts 14 and 15 (56%) was a viscous liquid: ir ($CHCl_3$) 1867 (m), 1790 (C=O), 1422, and 1182 cm^{-1} (SO_2); nmr (CCl_4) δ 1.15 (s, $-CH_3$), 1.42 (d, $HCCH_3$), 1.45 (s, $-CH_3$), 1.97 (m, $HCCH_3$), 2.40 [d, $HC(C_6H_5)CH-$)], and 7.15 (*m*, aromatic H).

Adduct 18b (13%) had mp 133–134°; ir ($CHCl_3$) 1750 (C=O), 1620 (C=C), 1412, and 1179 cm^{-1} (SO_2); nmr (CCl_4) δ 1.45

(32) It is necessary to remove all of the unreacted CSI (under reduced pressure) prior to chromatographic separation on silica gel. Any remaining CSI hydrolyzes on the silica gel and results in destruction of the *N*-chlorosulfonylimino ethers.

(33) At temperatures above 150° the character of the sample begins to undergo noticeable changes. On heating at 180° for 10 min lactams **9a** and **10a** undergo significant rearrangement to mixtures of isomeric compounds, the nature of which have not been fully investigated. As a result the melting points of **9a** and **10a** are not highly reproducible.

(s, 3 H), 1.60 (d, J = 6.5 Hz, 3 H), 2.33 (s, 3 H), 4.80 (q, J = 6.5 Hz, 1 H), 6.50 (broad s, 1 H), 7.17 (m, 5 H).

Adduct 21 (3.5%) had mp 118–120° (acetone–water); ir ($CHCl_3$) 1614 (C=C) and 1575 cm^{-1} (C=N); uv max (95% ethanol) 320.5 nm (ϵ 4600); nmr ($CDCl_3$) δ 1.54 (s, 3 H, CH_3), 1.66 (d, J = 6.5 Hz, 3 H, >CHC**H**$_3$), 2.39 (s, 3 H, =CC**H**$_3$), 5.41 [q, J = 6.5 Hz, 1 H, -C**H**(CH$_3$)O], 6.56 (br s, 1 H, =CH), and 7.30 (s, 5 H, aromatic).

Anal. Calcd for $C_{15}H_{16}ClNO_3S$: C, 55.29; H, 4.95. Found: C, 55.52; H, 5.28.

Lactam 18a (7%) had mp 174–175° (aqueous acetone); ir ($CHCl_3$) 3425 (NH), 1692 (C=O), and 1629 cm^{-1} (amide II and/or C=C); uv max (95% ethanol) 297 nm (ϵ 8400); nmr ($CDCl_3$) δ 1.36 (s, 3 H, CH_3), 1.33 (d, J = 6.3 Hz, 3 H, >CH-C**H**$_3$), 2.29 (s, 3 H, CH_3), 4.17 (q, J = 6.3 Hz, 1 H, >C**H**CH$_3$), 6.31 (br s, 1 H, =CH), 6.81 (br, 1 H, NH), and 7.20 (s, 5 H, aromatic H); mass spectrum m/e (calcd for $C_{15}H_{17}NO$, 227.132) 227.137.

Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.24; H, 7.48; N, 6.30.

Lactam 19 was obtained in <1% yield as a mixture with **18a** and was identified by comparison with the nmr spectrum of **19** derived by isomerization of **18a** (*vide infra*).

Lactam 20 (0.5%) had mp 192–193° (aqueous acetone); ir ($CHCl_3$) 1690 cm^{-1} (C=O); uv max (95% ethanol) 287.5 nm (ϵ 10,800); nmr ($CDCl_3$) δ 1.60 (d, J = 7.3 Hz, 3 H, CH_3), 2.08 (s, 3 H, CH_3), 2.48 (s, 3 H, CH_3), 5.13 (br s, 1 H, >CHN), 5.85 (br q, J = 7.3 Hz, 1 H, =CH), 6.30 (br, 1 H, NH), and 7.28 (s, 5 H, aromatic H).

Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.03; H, 7.50; N, 6.04.

Base-Catalyzed Hydrolysis of Mixture of 14 and 15.—The base-catalyzed hydrolysis of the mixture of **14** and **15** (65 mg) was effected as described in procedure B. The product was purified by column chromatography on silica gel (hexane), giving a mixture of **16** and **17** as a viscous liquid: ir ($CHCl_3$) 1690 cm^{-1} (cyclopropyl ketone); nmr (CCl_4) 0.83 and 0.94 [d's, J = 6.0 Hz, 6 H, -CH(CH$_3$)$_2$ of two isomers], 1.22 (m, 4 H, >CHCH$_3$), 2.0–2.6 [m, 3 H, CHC(=O)CH and CHC$_6$H$_5$], and 7.11 (s, 5 H, aromatic H); mass spectrum m/e (calcd for $C_{14}H_{18}O$, 202.136) 202.137; m/e (rel intensity) 202 (50.8), 159 (51.9), 131 (100.0), and 71 (49.0).

Iodine-Catalyzed Isomerization of 18a.—Approximately 40 mg of **18a** in 0.5 ml of deuteriochloroform was treated with a few crystals of iodine. After standing at room temperature for 24 hr, the conversion to **19** appeared complete. Work-up as described earlier afforded **19** as colorless crystals: mp 126° (aqueous acetone); ir 1685 cm^{-1} ($\nu_{C=O}$); uv max (95% ethanol) 318.5 nm (ϵ 17,300); nmr ($CDCl_3$) δ 1.23 (d, J = 6.3 Hz, 3 H, $-CH_3$), 2.21 and 2.49 (s, 3 H each, $-CH_3$'s), 4.58 (d of q, J = 1.7 and 6.3 Hz, 1 H, -C**H**(CH$_3$)N–], 6.68 (br s, 1 H, =CH), and 7.32 (s, 5 H, aromatic H).

Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 78.91; H, 7.51; N, 5.93.

Reaction Products Derived from 22 with CSI. Mixture of ketones 23 and 24 was a ~5:1 ratio of isomers in 30% isolated yield: ir ($CHCl_3$) 1690 cm^{-1} (C=O); nmr (benzene) δ 0.77 and 0.79 (d's, J ~ 6.2 Hz, ~3 H, >CHC**H**$_3$), 1.02 [d, J = 7.0 Hz, 6 H, -CH(C**H**$_3$)$_2$], 1.6 (m, 1 H, >C**H**CH$_3$), 1.98 (m, 1 H, >C**H**C$_6$H$_5$), ~2.65 (overlapping m, 2 H, O=CC**H**<); mass spectrum m/e (rel intensity) 202 (36.3), 159 (33.2), 131 (100.0), 71 (51.9), and 43 (91.3).

Lactam 25 (16–33%) was white needles: mp 168–170.5 (ether); ir ($CHCl_3$) 3450 (NH), 1690 (C=O), and 1630 cm^{-1} (C=C); uv max (95% ethanol) 258 nm (sh, ϵ 7500); nmr δ 1.60 (d, J = 7.0 Hz, 3 H, C**H**$_3$CH=), 1.81 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 4.98 (br s, 1 H, >CHN<), 5.25 (br q, J = 7.0 Hz, 1 H, =CHCH$_3$), 6.50 (br, 1 H, >NH), and 7.29 (s, 5 H, aromatic H); mass spectrum m/e (calcd for $C_{15}H_{17}NO$, 227.132) 227.131.

Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.31; H, 7.67; N, 6.16.

Adduct 27 (~0.3%) had ir ($CHCl_3$) 1575 cm^{-1} (C=N); nmr δ 1.68, 2.05, 2.43 (s, 3 H each, $-CH_3$'s), 5.48 (br q, 1 H, >CHO–), 6.09 (m, 1 H, =CH), 7.36 (s, 5 H, aromatic H).

Isomerization of 25.—A dilute chloroform solution of **25** (~40 mg) containing a few crystals of iodine was refluxed for 6 days. The usual processing gave in nearly quantitative yield the isomeric lactam **26** as a yellow solid: mp 169–170° (aqueous acetone); ir ($CHCl_3$) 1700 cm^{-1} (C=O); uv max (95% ethanol) 370 nm (ϵ 5800); nmr ($CDCl_3$) δ 1.16 (t, J = 7.5 Hz, 3 H, $-CH_2CH_3$), 2.25 and 2.50 (s, 3 H each, CH_3's), 2.56 (q, J = 7.5 Hz, 2 H, $-CH_2CH_3$), and 7.43 (s, 5 H, aromatic H).

Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.03; H, 7.50; N, 6.37.

Reaction Products Derived from 28 with CSI. Adduct 29 was a viscous liquid (51% isolated yield): ir ($CHCl_3$) 1871, 1846, 1831 (moderate intensity), 1794 (C=O), 1411, and 1165 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 1.21 (overlapping d, J = 5.4 Hz, 6 H), 1.47 [s, 6 H, >C(CH$_3$)$_2$], and 1.85 (br m, 2 H, >CHCH$_3$).

Adduct 30 (8.5% isolated yield) had ir ($CHCl_3$) 1625 (C=C), 1565 (C=N), 1365 and 1165 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 1.57 [d, J = 6.1 Hz, 3 H, -CH(CH$_3$)O–], 1.72 (d d, J = 7.3 and ~1.2 Hz, 3 H, =CHCH$_3$), 2.08 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3), 5.28 (br q, J = 6.1 Hz, CHO–), 5.68 (br q, J = 7.3 Hz, 1 H, =CH).

Adduct 31 (15.5% isolated yield) was a viscous oil: ir ($CHCl_3$) 1742 (C=O), 1630 (C=C), 1405, and 1159 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 1.49 [d, J = 6.5 Hz, 3 H, -CH(CH$_3$)N–], 1.68 (d, J = 7.4 Hz, 3 H, =CHCH$_3$), 1.94 (s, 3 H, CH_3), 2.39 (s, 3 H, CH_3), 4.65 (q, J = 6.5 Hz, 1 H, =CHN–), and 5.64 (q, J = 7.4 Hz, 1 H, =CHCH$_3$).

Mixture of keto amides 32a and 33a had mp 92–98°; ir ($CHCl_3$) 3507 and 3400 ($-NH_2$), 1695 (C=O), 1676 cm^{-1} (CO-NH$_2$); nmr ($CDCl_3$) δ 1.18 (distorted d, $J \cong 5.0$ Hz, 6 H, cyclopropyl methyls), 1.40 [s, 6 H, >C(CH$_3$)$_2$], 1.50 (m, 2 H), 2.13 (m, 1 H, >CHCO–), and 5.7 (s, 2 H, $-NH_2$); mass spectrum (calcd for $C_{10}H_{17}NO_2$, 183.127) 183.122; m/e rel intensity) 183 (3.1), 114 (6.2), 97 (100), 96 (2.6), 87 (29.0), 86 (9.1), and 69 (17.8).

Mixture of ketones 32b and 33b was a liquid: ir ($CHCl_3$) 1685 cm^{-1} (C=O); nmr (CCl_4) δ 1.04 [d, J = 7.0 Hz, 6 H, -CH(CH$_3$)$_2$], 1.12 (br s, 6 H, cyclopropyl methyls), 1.1–1.5 (br m, 3 H), and 2.11 [h, J = 7.0 Hz, 1 H, -C**H**(CH$_3$)$_2$]; mass spectrum m/e (calcd for $C_9H_{16}O$, 140.120) 140.121; m/e (rel intensity) 140 (8.2), 97 (100.0), 71 (4.4), 69 (11.0), 43 (14.6).

Lactone 34 was a liquid: ir (neat) 1750 (C=O) and 1643 cm^{-1} (C=C); nmr (CCl_4) δ 1.37 [d, J = 6.3 Hz, 3 H, -CH-(CH$_3$)O–], 1.68 (d, J = 7.2 Hz, 3 H, =CHCH$_3$), 1.92 (s, 3 H, $-CH_3$), 2.31 (s, 3 H, $-CH_3$), 4.71 (q, J = 6.3 Hz, 1 H, >CHO–), 5.47 (q, J = 7.2 Hz, 1 H, =CHCH$_3$).

Lactam 35 had mp 113–114° (ether); ir ($CHCl_3$) 3425 (NH), 1690 (C=O), and 1630 cm^{-1} (C=C); nmr ($CDCl_3$) δ 1.22 [d, J = 6.2 Hz, 3 H, -CH(CH$_3$)N–], 1.63 (d, J = 7.2 Hz, 3 H, =CHCH$_3$), 1.83 (s, 3 H, $-CH_3$), 2.34 (s, 3 H, $-CH_3$), 4.02 (q, J = 6.2 Hz, >CHN–), 5.42 (q, J = 7.2 Hz, 1 H, =CHCH$_3$), and 6.52 (br s, 1 H, NH).

Reaction Products Derived from 36 with CSI. Adduct 37 was a viscous liquid: 53% isolated yield; ir ($CHCl_3$) 1880, 1840 (medium), 1797 (C=O), 1415, and 1175 cm^{-1} (SO_2); nmr (CCl_4) δ 1.29 (m, 8 H, >CHCH$_3$), 1.48 (s, 3 H, $-CH_3$), and 1.50 (s, 3 H, CH_3).

Mixture of adducts 30 and 39 was a viscous liquid: ir ($CHCl_3$) 1630 (C=C), 1570 (C=N), 1370, and 1165 cm^{-1} (SO_2); nmr ($CDCl_3$) (in addition to the peaks of the major isomer **30**) δ 1.53 (d, J = 6.1 Hz), 1.84 (d, J = 7.3 Hz), 2.28 (s, 3 H, =C-CH$_3$), 2.53 (s, 3 H, =CCH$_3$), 5.35 (q, $J \cong 6$ Hz, >CHO–), and 5.81 (q, $J \cong 7$ Hz, =CHCH$_3$).

Mixture of adducts 31 and 41 was a viscous oil: ir ($CHCl_3$) 1745 (C=O), 1630 (C=C), 1410, and 1170 cm^{-1} (SO_2); nmr (CCl_4) (in addition to the peaks of the major isomer **31**) δ 1.49 (d, $J \cong 6$ Hz), 1.72 [d, $J \cong 7$ Hz, >CH(CH$_3$)N–], 2.14 (s, CH_3), 2.42 (s, CH_3), 4.54 (q), and 5.77 (q, =CHCH$_3$).

Keto amide 38a had mp 92.0–93.5° (ether); ir ($CHCl_3$) 3504 and 3397 ($-NH_2$), 1690 (C=O), 1677 ($-CONH_2$), 1605 (C=C), 1580 (amide II); nmr ($CDCl_3$) δ 1.13 (m, 8 H, >CH-CH$_3$), 1.41 [s, 6 H, C(CH$_3$)$_2$], 1.97 (m, 1 H, >CHCO), and 5.75 (br s, 2 H, $>NH_2$); mass spectrum m/e (calcd for $C_{10}H_{17}NO_2$, 183.123) 183.127.

Ketone 38b was a liquid: ir (CCl_4) 1685 cm^{-1} (C=O); nmr (CCl_4) δ 1.06 (br s, 3 H, >CHCH$_3$), 1.08 [d, J = 7.0 Hz, 6 H, -CH(CH$_3$)$_2$], 1.13 (br s, 3 H, >CHCH$_3$), 1.25 (m, 2 H, >CHCH$_3$), 1.66 (m, 1 H, >CHCO–), and 2.62 [h, J = 7.0 Hz, 1 H, -C**H**-(CH$_3$)$_2$]; mass spectrum m/e (calcd for $C_9H_{16}O$, 140.120) 140.121; m/e (rel intensity) 140 (9.0), 97 (100.0), 71 (13.0), 69 (12.3), 43 (18.5).

Mixture of lactones 34 and 40 was an oil: ir ($CHCl_3$) 1741 (C=O) and 1632 cm^{-1} (C=C); nmr (CCl_4) (in addition to peaks of the major isomer **34**) δ 1.36 (d, J = 6.3 Hz), 1.82 (d, $J \cong 7$ Hz), 2.13 (s, CH_3), 2.42 (s, CH_3), ~5.75 [q, -C**H**(CH$_3$)O–],

and 5.72 (q, $J \cong 7$ Hz, $=CHCH_3$); mass spectrum m/e (calcd for $C_{10}H_{14}O_2$, 166.099) 166.100.

Mixture of lactams 35 and 42 was an oil: ir ($CHCl_3$) 3430 (NH), 1689 (C=O), and 1634 cm^{-1} (C=C); nmr ($CDCl_3$) (in addition to peaks of the major isomer **35**) δ 1.22 (d, J = 6.2 Hz), 1.63 (d, J = 7.2 Hz), 2.07 (s, CH_3), 2.43 (s, CH_3), 4.28 [q, J = 6.2 Hz, $-CH(CH_3)N-$], 5.73 (q, J = 7.2 Hz, $=CHCH_3$), and 6.82 (br s, 1 H, NH); mass spectrum m/e (calcd for $C_{10}H_{15}NO$, 165.116) 165.112.

Registry No.—**6**, 4544-23-4; **7a**, 37817-10-0; **7b**, 37817-11-1; **8a**, 37817-12-2; **8b**, 37817-13-3; **9a**, 37817-14-4; **9b**, 37817-15-5; **10a**, 37817-16-6; **10b**, 37817-17-7; **11**, 37817-18-8; **12**, 37817-19-9; **13**, 33530-27-7; **14**, 37817-21-3; **15**, 37817-22-4; **16**, 37817-23-5; **17**, 37817-24-6; **18a**, 37817-25-7; **18b**, 37817-26-8; lactam **19**, 37817-27-9; adduct **21**, 37817-29-1; **22**, 33530-26-6; **23**, 37817-31-5; **24**, 37817-32-6; **25**, 37817-33-7; **26**, 37817-34-8; **28**, 37817-36-0; **29**, 37817-37-1; **30**, 37817-38-2; **31**, 37817-39-3; **32a**, 37817-40-6; **32b**, 37817-41-7; **33a**, 37817-42-8; **33b**, 37817-43-9; **34**, 37817-44-0; **35**, 37817-45-1; **36**, 37817-46-2; **37**, 37893-77-9; **38a**, 37817-48-4; **38b**, 37817-53-1; **39**, 37817-47-3; **40**, 37817-51-9; **41**, 37817-49-5; **42**, 37817-28-0; CSI, 1189-71-5.

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Carbon-13 Nuclear Magnetic Resonance Spectroscopy. The Spectra of the Linear Alkynes[1]

DOUGLAS E. DORMAN, MANFRED JAUTELAT, AND JOHN D. ROBERTS*

Contribution No. 4509 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109

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The ^{13}C chemical shifts of a selection of linear alkynes are collected and correlated with structure. A system of empirical rules by which the ^{13}C nuclear magnetic resonance spectra of such compounds can be predicted is derived. The failure of the current point-dipole approximation to predict correctly the shifts due to the anisotropy of the triple bond is discussed.

Carbon-13 nuclear magnetic resonance (^{13}C nmr) spectra have been reported for a number of linear alkynes.[2-6] In most cases,[2-5] only the chemical shifts of the sp-hybridized carbons were reported, and in all cases spectra were measured using the adiabatic, rapid-passage technique, which generally yields experimental uncertainties of 0.5 ppm. While accuracy of this magnitude is adequate for many applications,[6] it is not sufficient to identify the more subtle chemical-shift differences associated with changes in substitution in remote sites in the molecule. Because such information is important in applications of ^{13}C nmr spectroscopy to problems in structure elucidation,[7] we have undertaken a brief survey of ^{13}C spectra of linear alkynes using the absorption mode and spectrum averaging. The present paper describes the results of this survey and compares them to those reported earlier.

Experimental Section

Carbon-13 chemical shifts were measured under conditions of full proton decoupling on the Varian digital frequency sweep spectrometer described previously.[8] Chemical shifts were measured relative to internal 1,4-dioxane and were then referenced to external carbon disulfide using the relation $\delta_{CS_2} = \delta_{1,4\text{-dioxane}} + 126.2$. Regression analyses were performed on an IBM 360/75 computer with the aid of a standard subroutine for stepwise multiple regression analysis.[9]

Results

The extant data for the linear alkynes and alkadiynes are presented in Table I. The spectrum of 1,7,13-tetradecatriyne[10] is also included for comparison. For the octynes, data from earlier workers and from these laboratories are both included in Table I. It is obvious that there are substantial differences between the spectra obtained by dispersion[6] and absorption modes. Indeed, the differences are often greater than the experimental errors of the two methods. These disparities are possibly partly due to solvent or concentration effects. The earlier data[6] were derived from neat solutions, while solutions in 1,4-dioxane were used in the present study. Throughout the remainder of this paper, only our own data for the octynes will be considered.

The spectra of the various alkynes are compared to those of the analogous alkanes in Table II. The values in this table were obtained by subtracting the shifts of the alkane from those of the alkyne in each case. From Table II it is evident that, within any particular subgroup of linear alkynes, the sp-hybridized carbons are shifted downfield from their positions in the saturated alkane by quite constant amounts. Thus, in the 1-alkynes, the terminal sp carbon is 54.5 ppm downfield from the corresponding methyl, while the other unsaturated carbon is about −61.0 ppm

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